
Review of environmental effects of oxybenzone and other sunscreen active ingredients



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With increasing awareness regarding the risks of sunburn, photoaging, and skin cancer, the use of sunscreens has increased. Organic and inorganic filters are used in sunscreen products worldwide. Concerns have been raised regarding the environmental effects of commonly used organic ultraviolet (UV) filters, including oxybenzone (benzophenone-3), 4-methylbenzylidene camphor, octocrylene, and octinoxate (ethylhexyl methoxycinnamate). Studies have identified UV filters such as oxybenzone, octocrylene, octinoxate, and ethylhexyl salicylate in almost all water sources around the world and have commented that these filters are not easily removed by common wastewater treatment plant techniques. Additionally, in laboratory settings, oxybenzone has been implicated specifically as a possible contributor to coral reef bleaching. Furthermore, UV filters such as 4-methylbenzylidene camphor, oxybenzone, octocrylene, and octinoxate have been identified in various species of fish worldwide, which has possible consequences for the food chain. As dermatologists, it is important for us to continue to emphasize the public health impact of excessive sun exposure and advise our patients about proper photoprotection practice, which consists of seeking shade, wearing photoprotective clothing (including hats and sunglasses), and applying appropriate sunscreens. (*J Am Acad Dermatol* 2019;80:266-71.)

Key words: benzophenone; butyl methoxydibenzoylmethane; ethylhexyl methoxycinnamate; ethylhexyl salicylate; 3,4-methylbenzylidenecamphor; nonmelanoma skin cancer; octocrylene; oxybenzone; octyl methoxycinnamate; sunscreen; ultraviolet radiation.

Skin cancer is the most common malignancy in the United States.¹ Nonmelanoma skin cancer affects millions of Americans annually, with increasing incidence of both basal and squamous cell carcinomas.² Ultraviolet (UV) radiation is a main risk factor for skin cancer development, as well as for erythema and photoaging. With increasing awareness regarding skin cancer, photoprotection has been widely advocated; sunscreen use is an integral part of photoprotection.

The active ingredients of sunscreens are divided into inorganic (physical) and organic (chemical) filters. Inorganic filters include titanium dioxide and zinc oxide, which reflect and refract UV photons; nanosized titanium dioxide also absorbs UV. Organic filters are designed to absorb UV A, UV B, or both. Aside from being used in sunscreen, several

Abbreviations used:

4-MBC:	4-methylbenzylidene camphor
ppb:	parts per billion
UV:	ultraviolet
WWTP:	wastewater treatment plant

UV filters, namely, oxybenzone (benzophenone-3), 4-methylbenzylidene camphor (4-MBC), octocrylene, and octinoxate (ethylhexyl methoxycinnamate), are used in cosmetics, shampoos, fragrances, and flavors and also as photostabilizers in personal products and plastics.^{3,4} With such wide applications, it is no surprise that the US Centers for Disease Control and Prevention has suggested that approximately 96.8% of the US population is exposed to oxybenzone.^{4,5} It should be noted that 4-MBC is an

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approved UV filter in the European Union but is not a listed filter in the US Food and Drug Administration monograph.

Researchers have examined the impact of these organic filters. In vitro, oxybenzone has antiandrogenic as well as proestrogenic and antiestrogenic effects.⁶ Oxybenzone, avobenzone (butyl methoxydibenzoylmethane), homosalate, octyl dimethyl-*p*-aminobenzoic acid (padimate O), and octinoxate increased cellular proliferation of MCF-7 breast cancer cells in vitro. Additionally, 4-MBC induced the pS2 protein (a protein regulated by estrogen) in MCF-7 cells; the effects were blocked by using an estrogen antagonist, which highlights the hormonal regulation of this process. In rats, 4-MBC and octinoxate applied topically and administered

orally led to increased uterine weight.⁷ A human study with 32 patient volunteers (men and postmenopausal women) examined the hormonal effects of systemic absorption of oxybenzone, 4-MBC, and octinoxate. The volunteers applied 2 mg/cm² of sunscreen with 10% active ingredients (1 sunscreen formulation for each of the active ingredients) over their entire body for 4 days. Levels of luteinizing hormone and follicle-stimulating hormone unchanged; however, the male patients had minor changes in their levels of other sex hormones, including testosterone, estradiol, and inhibin B. These changes were thought to be biologically inconsequential.⁸ In humans, the rate of systemic absorption of oxybenzone has been estimated as 1% to 2% with topical application,^{5,8-14} though others have reported the rate to be as high as 10%.¹³ Oxybenzone has the highest percutaneous absorption and has been identified in human urine, serum, and breast milk^{3,4,6,15-18}; however, there have not been any reported toxic effects in humans since 1978, when it became commercially available.^{5,11} A mathematic modeling study estimated that it would take 35 to 277 years of daily use for humans to achieve the equivalent serum levels of oxybenzone seen in rat models.⁵

Effects on the environment have become a pressing topic. UV filters have been identified in water sources worldwide,^{6,19-29} with oxybenzone noted as the filter most frequently detected in the highest concentrations.²³ Organic filters enter the environment through different mechanisms. They

are absorbed percutaneously and excreted in the urine, which enters the plumbing. Only approximately 4% of the applied dose was excreted in the urine,¹⁴ leaving the majority of the filter on the skin to be washed off in natural water sources or in the shower—with all such water entering the water supply.^{3,4} Manufacturing and waste runoff produced

from factories also places organic filters into the water supply.^{3,4} In fact, 1 study found higher concentrations of oxybenzone in the water supply in metropolitan areas with both commercial and industrial water runoff than at recreational water sites.³ Organic filters are prevalent in waste from manufacturing facilities, particularly those for sunscreens and cosmetics. With growing awareness of the importance of photoprotection and increasing use of sunscreens,

it is no surprise that these filters have been identified broadly in our water sources. In this review article, we will examine the prevalence of UV filters in water, as well as their proposed environmental impact. To conclude, we will propose potential solutions and alternatives.

WATER SOURCES

Wastewater treatment plants (WWTPs) are critical in the water recycling process. Water utilized by humans passes through these facilities for treatment before re-entering rivers and streams. WWTPs worldwide have been tested for UV filters in their influent (incoming water sources) and effluent (water that has been treated). In Brazil, oxybenzone, ethylhexyl salicylate, octinoxate, and octocrylene were identified in raw and treated water.²⁶ Oxybenzone, 4-MBC, octinoxate, and octocrylene were all found in WWTPs in Switzerland,²² with oxybenzone concentrations of 69 g per 10,000 people per day.²⁷ Studies performed in Korea, China, the United States, Japan, and Thailand yielded similar results.²⁹

WWTPs have difficulty treating organic filters on account of their innate chemical properties. WWTPs were designed to treat particulates in the water. UV filters, however, have low water solubility, high lipophilicity, and a high organic carbon-water coefficient, which makes it challenging for WWTPs to remove them.³⁰ It has been shown that

CAPSULE SUMMARY

- Organic ultraviolet filters have been identified in water sources and aquatic animals worldwide.
- Oxybenzone has been implicated in coral reef bleaching, which prompted Hawaiian state legislature to pass a bill banning certain sunscreens.
- Health care providers should encourage photoprotection including shade, photoprotective clothing, and applying appropriate sunscreens on exposed skin.

oxybenzone was not sufficiently removed by the treatment process,^{21,26} allowing it to re-enter the water supply as the effluent.

The concentrations of organic filters in different water sources have seasonal variations, with higher concentrations in the summer.^{22,29,31} In a study done in Korea, an increase in UV filters in the WWTP effluent of more than 25% during the summer was reported.²⁹ This suggests an impact of human behavior on water concentrations that is due both to recreational activities and the likely increased manufacturing to meet the increased demand. Furthermore, concentrations of filters in the water were higher in densely populous areas.^{3,19} Interestingly, UV filters have been identified in the Arctic, which suggests that water currents are dispersing the filters beyond their initial deposition. This has potential significant implications for the environment.³

Aside from being present in natural water sources, UV filters have been identified in chlorinated water, such as that in swimming pools. Organic filters can react with chlorine to create hazardous by-products called brominated transformation products.^{3,32,33} A study examined chlorinated salt water pools for the presence of dioxybenzone, oxybenzone, avobenzene, octinoxate, and octocrylene; the only UV filter studied that did not react with chlorine was octocrylene.³³ Compared with unchlorinated controls, chlorinated oxybenzone led to a higher rate of cell death when studied in vitro.³² The ultimate human health impact of chlorinated by-products will require more studies.

CORAL REEFS

Coral reefs are a critical component of our environment, supporting as many as 1 million species of fish, invertebrates, and algae.³⁴ Coral belong to the *Cnidaria* family, which are soft bodied animals that engage in symbiosis with algae (zooxanthellae). Zooxanthellae live on coral. Their photosynthesis gives coral energy, and the algae itself provides the coral's vibrant colors. As coral grows, it forms branching structures culminating in reefs. When coral reefs face oxidative stress from warming ocean temperatures and/or pollutants, they expel algae from their surface, turning the coral white (also known as bleaching). This process often leads to the coral's demise.

Coral reefs are endangered, with warnings and/or watches imposed by oceanic societies worldwide. The reasons for their endangerment are multifactorial. Arguably, the most important factor is warming ocean temperatures; however, additional factors include pollutants and decreasing ocean salinity.³⁵

Specifically, oxybenzone has been named a threat to coral reefs worldwide. It has been estimated that as much as 14,000 tons of sunscreen, some containing as much as 10% oxybenzone, is released into coral reef areas annually.^{34,36} Ninety percent of snorkeling and diving sites occur on 10% of the world's reefs,³⁴ which puts approximately 10% of global reefs and up to 40% of coastal reefs at risk for coral bleaching.³⁴

Because coral reefs are so diverse, species will be affected differently by organic filters. Juvenile coral (also known as coral larva) is very susceptible to pollutants, as are newly settled coral reefs.³⁶ In contrast, coral that grows more slowly is more resistant, as these species have lower bioaccumulation rates.

Researchers utilized *Chlamydomonas reinhardtii* (a species of green algae) as a model to study the effects of oxybenzone. In vitro, *C reinhardtii* was exposed to varying levels of oxybenzone, with the lowest concentrations akin to those encountered in the environment (0.01-0.1 parts per billion [ppb]) and the highest up to 5000 ppb. The higher concentrations of oxybenzone resulted in decreased chlorophyll content and overall growth, though it is notable that these concentrations were higher than the currently measured environmental levels.³⁷ In Okinawa, Japan, oxybenzone levels are elevated at sites of public swimming beaches (0.4-3.8 parts per trillion), and these levels continue to remain elevated as far as 600 m away, demonstrating the role of diffusion and ocean currents in dispersal of chemicals. Concentrations at reefs were higher than those at beaches or rivers.³¹

Danovaro et al proposed a mechanism for coral reef bleaching, according to which UV filters activate coral viruses, which culminates in oxidative stress, expulsion of symbiotic algae, and thus coral bleaching.^{3,34,38} In vitro, at concentrations of 33 to 50 parts per million, oxybenzone induces coral reef bleaching and death.^{3,38} The measured lethal concentration 50 for 7 different species of coral cells in vitro ranged from 8 to 340 ppb.³⁶ Concentrations of oxybenzone in the ocean surrounding US Virgin Islands and Hawaiian Islands ranged from 75 to 1400 ppb and 0.8 to 19.2 ppb, respectively.^{3,36} In Chile and Colombia, the oxybenzone level was elevated in sediment from nearby coral reefs, with levels up to 2.96 ppb in Chile and 5.38 ppb in Colombia. In Colombia, octinoxate levels reached 47 ppb and levels of 4-MBC reached 17.2 ppb. Clearly, these values are in the low to zero toxicity ranges for coral bleaching.³⁹

FOOD CHAIN

UV filters have been studied in fish and mammals. In rats, 4-MBC interferes with sexual behavior and reproductive practices.^{18,29} In zebra fish, octocrylene alters development in brain and liver.³⁰ In rainbow trout and Japanese rice fish (medaka), laboratory studies demonstrated that exposure to high concentrations of oxybenzone led to decreased egg production, with significantly fewer hatchings, as well as induction of vitellogenin protein in males (a precursor of the egg yolk found only in females).⁴⁰ The presence of vitellogenin in male fish suggests possible feminization, which has obvious implications for reproduction.

In Switzerland, white fish, roach, and perch found in lakes had low but detectable amounts of UV filters, mostly 4-MBC.²² In Norway, cod liver contained UV filters. Octocrylene was the most commonly identified filter (found in 80% of specimens), with oxybenzone being the next most common (50%).²⁸ White fish also contained oxybenzone and octinoxate.²⁸ In Spain, similar UV filters were identified in white fish, rainbow trout, barb, chub, perch, and mussels.^{3,20}

The concentrations present in fish were low; however, the concepts of bioaccumulation and biomagnification must be considered. Bioaccumulation describes the phenomenon whereby chemicals reach higher concentrations in organisms over time than in their environment. Brausch and Rand examined bioaccumulation and found that oxybenzone levels were higher in fish than in water.^{3,27} Biomagnification refers to the concept that chemicals become more concentrated and detrimental as one moves higher up the food chain. Chemicals are not removed or broken down by lower organisms; thus, when an animal ingests these lower-order organisms, it obtains a higher concentration of the chemical. This suggests a possible negative implication for humans who ingest seafood, although at this time no clear adverse effects in humans have been reported.⁴¹

SOLUTIONS

Given the growing concerns regarding UV filters present in the environment, public and government agencies have been searching for solutions. Legislation has been proposed to ban chemicals that have affected our food supply.^{3,42} On May 1, 2018, the Hawaiian state legislature passed a bill that bans the sale and distribution of sunscreens containing oxybenzone and octinoxate. At the time of writing of this review, the bill was awaiting the signature of Governor David Y. Ige.⁴³ If the bill is

signed or proceeds without a veto, the law will go into effect in 2021. Additional states have considered similar legislation.

Several aquatic parks have published literature to educate the public regarding the risk of organic filters for the marine environment. Xel-Há in Mexico advises tourists to travel with chemical-free sunscreen when visiting their park,⁴⁴ and the US National Park Service published an educational pamphlet stating “Remember if it’s on your skin, it’s on the reef. Be reef friendly! Reduce the amount of sunscreen you leave behind....”³⁴ Hawaiian Airlines has joined the cause by showing a documentary about reef bleaching during flights and distributing reef-safe sunscreen (containing only inorganic filters).⁴⁵

Photoprotection should include seeking shade when outdoors; wearing photoprotective clothing, including swimwear, wide-brimmed hats, and sunglasses; and applying sunscreens only on exposed areas. Practicing photoprotection with the aforementioned guidelines and applying sunscreens with inorganic filters (titanium dioxide and zinc oxide) are an alternative means of protecting oneself from UV radiation.

Aside from limiting continued leaching of UV filters into the environment, means of optimizing their removal from the water supply have been explored. Studies have been done with *Cyperus alternifolius* L, which is a common wetland plant that absorbs oxybenzone into its root system and accumulates the chemical in its tissues. The plant ultimately converts oxybenzone to chemical conjugates with lower toxicity. This mechanism was evaluated as a means of possibly removing oxybenzone from the environment, with the caveat that these plants would need to be extracted before undergoing natural decay.⁴⁶

CONCLUSION

With the known effects of UV radiation on erythema, photoaging, and development of skin cancer, photoprotection is paramount. However, we must also take into account the impact of our efforts on the environment. UV filters have been identified in many water sources; they are extremely difficult to remove by using traditional WWTP practices. With continued use of organic filters, one can surmise that concentrations in our water sources will continue to rise. The effect on coral reefs is clearly multifactorial; however, at increasing concentrations, UV filters may play a more instrumental role in bleaching. Furthermore, increasing ocean concentrations will accentuate bioaccumulation and biomagnification, ultimately

raising potentially negative consequences in humans. Fortunately, the currently detected levels in the environment have been in the lower toxicity ranges for the species of coral studied *in vitro*, and there have been no identifiable toxic effects on humans.

It seems clear that with this growing body of evidence of the negative impact of organic UV filters in our environment we should actively explore alternative forms of photoprotection and novel water filtration methods. The effects of inorganic filters on the environment is still being studied, but at this time, physical blockers are recommended as photoprotection alternatives. The concern about the environmental impact of organic UV filters should not detract from educating the public on the importance of photoprotection, namely, to seek shade, wear photoprotective clothing and swimwear when outdoors, and apply appropriate sunscreens on sun-exposed areas. This would allow us to protect our skin from the deleterious effects of sunlight and, at the same time, protect our environment.

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